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Summary Report

Development of Ultra Refractory Materials

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(Unclassified)

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ABSTRACT

Room temperature investigations of various physical, mechanical and electrical properties of solid solutions of tantalum carbide and zirconium carbide showed no evidence of discontinuous changes indicating new phases or compound formation after a wide variety of annealing treatments. Emissivity studies, however, indicate the probable existence of high temperature phases of both tantalum carbide and zirconium carbide, though not of the solid solutions. The reported increase in melting temperature of ZrC-TaC solid solutions has been confirmed.

Additional work to resolve the problem of consistently low melting temperatures was deferred by the sponsor due to the urgency of the radome thermal shock problem.

Preliminary studies indicate that Lithafrax® low expansion lithium aluminum silicate has a thermal shock resistance factor more than twice as great as Pyroceram® 9606 and more than four times as great as alumina. Electrical properties, with the possible exception of dissipation factors, are within acceptable limits. Similar lithium aluminum silicate compositions with effectively zero expansion are known. These would, therefore, have infinite thermal shock resistance factors.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (cont'd)

I. INTRODUCTION

This Summary Report, covering the period from 1 November 1960 through 31 October 1961, is the fourth such summary report to be issued under Contract NOrd-17175 which was initiated in August, 1956. Research covered in this last report was devoted to a study of the mixed carbide system (ZrC-TaC) and to a preliminary investigation of thermal shock resistant materials for radome applications.

Mr. George B. Butters, Code RMGA, has been the project engineer since the inception of this research contract.

II. SUMMARY

Major emphasis has been devoted during the first nine months of the report period to a fundamental study of the mixed carbide systems, consisting of mixtures of monocarbides of the group IV and V metals. Specifically, an investigation of the properties of solid solutions of zirconium carbide and tantalum carbide was undertaken in an effort to explain certain anomalies such as the increased melting temperatures, increased high temperature strength, and increased creep resistance observed in these solid solutions. It was hoped that the study of the properties of a range of compositions after various annealing treatments would provide evidence of compound formation.

No significant changes could be found in Young's modulus of elasticity, microhardness, lattice spacing, or electrical resistivity after the annealing treatments. Recently, Engelke[1] reported that no maximum in the solid solution melting point was found in the systems HfC-NbC and HfC-TaC. He further attributes Agte's[2] results to a deficiency in carbon in the tantalum carbide studied. Robins[3] discusses the same problem on the basis of the electronic configuration, and states that the composition corresponding to 4.8 electrons per carbon atom yields the most stable, hence the highest melting composition.

Our observations, as well as the aforementioned papers, did not clarify the situation. It was decided, therefore, to remeasure the melting temperatures in an attempt to prove to our own satisfaction whether the melting point increase really exists.

Calculated spectral emissivities showed a reversible change on heating the pure carbides. This change in emissivity is accompanied by a marked increase in resistivity and an apparent density decrease. The measured melting temperatures are lower than the reported values. The cause of the low melting temperatures, due probably to failure to apply necessary temperature corrections, has not been resolved. Independent

measurement of the melting temperature of the tantalum carbide showed it to melt at 7030°F (3890°C)[4], which is the generally accepted value. This shows that our low reported temperatures are the result of an error in temperature corrections.

The problem of thermal shock in ceramic materials recently having become of the utmost importance in certain radomes, a survey was started to determine whether radome materials with improved thermal shock resistance could be developed. The recent generation of missiles subject radome materials to aerodynamic heating rates which cause even thermal shock resistant bodies, such as Pyroceram® 9606, to fail catastrophically. It was, therefore, the immediate objective of this program to investigate the problem of thermal stresses in radome structures and to suggest a possible solution.

Lithafrax® low expansion lithium aluminum silicate ceramics have been shown to have thermal shock resistance factors twice as great as Pyroceram® 9606 and more than four times as great as alumina. Other lithium aluminum silicate compositions have been prepared which show zero thermal expansion coefficients, therefore infinite resistance to thermal shock. The exact electrical properties of these materials have not been measured; however, preliminary measurements indicate that properties within the limits of acceptance can be obtained.

II. WORK PROGRESS

A. Carbides

1. Background

As early as 1930, Agte[2] reported that the solid solution composition 4TaC-ZrC had a melting temperature higher than that of either constituent carbide. This melting point increase in a solid solution is without parallel in solid solutions where no compound formation occurs[5].

Early x-ray diffraction studies showed that binary mixtures of monocarbides of the Groups IV and V metals formed complete solid solution series with the exception of the system ZrC-VC[6], and that the lattice parameters show a continuous, essentially linear relation, indicating that these are true, simple solid solutions[7]. More recent work by Kovalskii and Petrova[8], however, showed that the systems are not as simple as had been reported. For example, the solid solution of equimolar amounts of TiC and ZrC is stable only above 3810°F (2100°C), disproportionating into 3:7 and 3:1 solid solutions when annealed at lower temperatures.

Quite recently Engelke[1] reported that no increase in the solid solution melting points exist in the systems HfC-NbC and HfC-TaC as reported by Agte[2]. He further attributed the reported increase in melting temperature to a deviation from stoichiometry in the TaC which Agte studied. Additional evidence for the non-stoichiometry of TaC is presented by Robins[3], who was unable to prepare the stoichiometric carbide in the presence of excess carbon. Reactions of tantalum filaments with excess methane or tantalum solutions in iron or aluminum with graphite powder yielded a material having a composition of $TaC_{0.96}$. This material, furthermore, lost carbon on heating above 4530°F (2500°C).

It was decided, therefore, to investigate the system ZrC-TaC with the object to determine whether the melting point increase really exists and to discover whether or not compound formation has taken place.

2. Preparation of Solid Solutions

In order to obtain the maximum homogeneity with a minimum handling of the hard carbides, the finely-powdered oxides were first carefully blended together, then blended with finely-powdered thermatonic carbon (Thermax®) and finally with a dilute solution of polyvinyl alcohol (PVA), cold pressed and dried. Each composition was fired at 2910°F (1600°C) for two hours then for one hour at 4350°F (2400°C) in an argon atmosphere. X-ray diffraction patterns of the reacted carbides showed single phase carbides or carbide solid solutions.

Typical spectrographic analyses of the reactants are given in Table No. I.

3. Preparation of Test Specimens

Each reacted carbide powder, after crushing and ball milling to -325 mesh was hot pressed to a billet of greater than 80 percent of theoretical density (calculated on the basis of simple volume additions). Test specimens were diamond-sawed from the hot pressed billets as required.

4. Annealing

Each composition was subjected to the same thermal conditions. After hot pressing, diamond sawing, and polishing, the samples were subjected to four-hour annealing cycles at 3810°F (2100°C), 3270°F (1800°C) and 2730°F (1500°C). To minimize any effect of reaction between the samples and carbonaceous furnace atmospheres, each bar was repolished after annealing to remove any reaction products before remeasurement of physical properties.

5. Lattice Parameters

X-ray diffraction showed each composition to consist of a single phase carbide after synthesis from the oxides. The (200) lattice spacings, plotted against the composition showed a continuous essentially linear relation as previously reported by Norton[6] (Figure 1). After each annealing treatment the carbides were reexamined. No evidence of disproportionation, formation of super lattice (disorder-order transformation), or shift in the lattice spacings could be detected.

In order to obtain the greatest accuracy in measuring lattice spacings an internal standard was included in all samples. The internal standard chosen for these measurements was ZrC, calibrated previously against a rock salt primary standard.

6. Microhardness

Measurements of microhardness of carbides after hot pressing and after subsequent annealing treatments generally showed a slight decrease in hardness with decreasing annealing temperature (Table No. II). No separations, indicating disproportionation or compound formation, were observed.

7. Electrical Resistivity

The electrical resistivity of each bar was measured as sawed from the hot-pressed billet and again after each annealing treatment. The data (Table No. III) show no significant changes with annealing treatment, the maximum change being 2.4 percent from the average. It is notable, however, that a maximum resistivity is reached in the range of the composition $ZrC \cdot 2TaC$ (Figure 2).

8. Young's Modulus

The transition from disordered to ordered structure or from mixture to compound is accompanied by a change in modulus of elasticity (Young's Modulus). After hot pressing and after subsequent annealing operations the Young's modulus (for each bar) was measured using the sonic method. Table No. IV lists the measured values of Young's modulus, as well as those values corrected to zero porosity.

No significant changes in Young's modulus were observed as a result of annealing. In addition, the plot of Young's modulus, corrected for porosity, as a function of composition does not show deviations, which would be expected if a compound were formed (Figure 3).

9. Melting Studies

Since all evidence pointed to the existence of a complete, stable solid solution series between the two carbides, TaC and ZrC, the next study was to attempt to prepare very pure samples of the carbides and to redetermine their melting temperatures to prove to our own satisfaction whether the melting point increase really exists.

a. Refractory Metals

In order to obtain information on the degree of reproducibility which might be obtained with the melting point apparatus (Figure 4), several samples of refractory metal sheets, tungsten, tantalum, molybdenum and niobium, were fused by direct resistance heating. Temperatures were measured on flat surfaces and corrected for emissivity and window reflections (Table No. V). Additional samples, bent into "V"-shape heaters were measured in a similar way, but not corrected for emissivity since a partial "black body" was obtained. These data are summarized in Table No. V.

The degree of precision is excellent especially with the "V"-shape specimens in which partial "black body" conditions exist. The averages and deviations are listed in Table No. VI.

Except for a possible error in the spectral emissivity reported in the literature, no explanation for the consistently low melting temperatures is available. Complete analysis of the metals for contaminants showed no impurities in amounts large enough to affect melting temperatures significantly. The precision and reproducibility of data, however, shows that relative temperatures should be sufficiently accurate to provide the information desired in the melting point study of the ZrC-TaC system.

b. ZrC-TaC System

A complete melting point study has been made on carbide test bars (3 x 1/8 x 1/8 inches) heated by passing a current directly through them. Apparent melting temperatures as reported are those at which first droplets of liquid were observed. Figure 5 shows typical ZrC bars before and after melting.

In order to assure a reproducible degree of "black body" conditions, each bar was ultrasonically drilled at its midpoint to provide a 1/64 inch diameter hole, 3/32 inch deep. The depth to diameter ratio of six, together with a rounded bottom, provided an effective "black body" on which to measure the internal temperature of the sample bars.

The measured temperatures even after applying known corrections for window absorption (Appendix A) were consistently low. No reference standard for calibration in the 5430°F (3000°C) plus range is available. Analyses were examined for a possible explanation to these low melting temperatures. The results of analyses showed that frequently samples of near stoichiometric composition melted as low as those which varied considerably from the theoretical composition.

The fact that melting temperatures from lot to lot of a particular carbide composition are quite reproducible lead to the conclusion that the actual melting temperatures were probably quite close to the reported values while the chemical analyses were not reliable. Recent checks showed that coprecipitation had in fact been confusing the analyses.

Sample tantalum carbide bars were sent for independent melting point studies at the Aerojet-General Corporation. The melting temperature which was reported (7030°F (3890°C))[4] confirms the fact that an error in temperature correction is responsible for the consistently low reported temperatures.

The melting temperatures, listed in Table No. VII, were, therefore, used for comparison. Though not absolute, these reported temperatures are sufficiently accurate relative to one another to demonstrate the presence of a maximum which is what the investigation was to show.

Figure 16 shows a plot of melting temperature versus composition and does in fact show the melting point maximum in the tantalum-rich region as reported originally by Agte[2].

Samples of tantalum carbide, zirconium carbide and their solid solutions after fusion were examined metallographically and by microhardness measurements as well as by x-ray diffraction. No evidence of new phases in the fused "button" were found.

c. Emissivity Studies

During the preliminary melting studies of direct resistance heated zirconium carbide bars, a marked change was noted at temperatures in excess of 3810°F (2100°C). Without a change in the applied voltages, a rapid increase in temperature, as much as 900°F (500°C), was noted. A zone could be observed to spread along the length of the bar, followed by the previously mentioned apparent temperature increase.

By measuring surface temperatures on areas polished with 400 grit diamond wheels and the internal or black body temperature, it was possible to calculate an approximate value for spectral emissivity. All temperatures were measured by means of a Leeds and Northrup optical pyrometer at a wave length of approximately 0.65 microns.

Subsequent experiment showed that not only is there a marked change in emissivity but that the actual temperature of the bar increases, accompanied by a decrease in resistivity of the sample bar.

Numerous zirconium carbide bars were examined during both heating and cooling cycles. The results of these observations show that at 4000°F (2200°C) a change in the nature of the zirconium carbide bar occurs accompanied by a decrease in spectral emissivity and a decrease in resistivity. The change is reversible, with both resistivity and emissivity returning to their original values. The transformation shows a hysteresis effect of nearly 900°F (500°C) which is not time dependent (Figure 7).

An additional observation is that the bars on heating through the range of 3630-4530°F (2000-2500°C) frequently split lengthwise, presumably due to an increase in volume accompanying the transformation (Figure 6). This volume increase has not been studied further.

A similar, though less sharply defined, change has been observed with tantalum carbide, but not with any of the solid solution compositions in the tantalum carbide-zirconium carbide series (Figures 8 through 15). Since these observations were made, a report describing similar observations made by General Electric on tantalum carbide has been released[9].

10. Conclusions

No evidence of compound formation in the series ZrC-TaC has been found. The melting point increase has been confirmed, while a maximum in electrical resistivity in the tantalum-rich region has been observed.

Spectral emissivity data shows evidence for a high temperature crystal form of both zirconium carbide and tantalum carbide, but not for solid solutions of these carbides. The crystallographic change, apparently a low-high inversion rather than a complete structural rearrangement, is accompanied by a volume increase and a decrease in electrical resistivity.

B. Radome Materials

1. Background

Velocities of many missiles which rely on radar and on infrared detection for directional control are such that plastics and glass are no longer adequate for use as radomes or IR domes. More refractory materials such as alumina, Pyroceram®, and fused silica have excellent electrical properties but suffer from thermal shock fracture. Flight patterns are such that the radomes are heated from ambient temperature to temperatures in excess of 1000°F in a matter of seconds. Thermal gradients set up within the radomes cause fracture of even such materials as Pyroceram® 9606.

A program was initiated to examine new thermal shock resistant materials for radome applications and compare them with the generally accepted candidate materials: alumina, Pyroceram® 9606, and slip cast fused silica. These were obtained from Gladding McBean, Corning Glass Works, and Georgia Institute of Technology, respectively.

Thermal shock resistance of a structure is related to several general factors such as heat pulse (magnitude and geometry), structural configuration (size and shape), and physical properties of the structural material itself. The heat pulse and structure are defined by the size, shape and performance of the missile. The factor to be considered, therefore, is the so-called "thermal shock resistance factor" of the ceramic material.

Many thermal shock resistance factors have been postulated, based on the factor $S/\alpha E$. In this case S is tensile strength, α is the coefficient of thermal expansion and E is Young's modulus of elasticity. It is on the basis of this factor ($S/\alpha E$) that materials are compared. Thermal shock testing was not carried out due to the termination of the contract.

2. Physical Properties

a. Strength

Test bars (3 x 1/2 x 1/4 inches) were broken using three-point loading, in air at several temperatures. Since no method is available to obtain reliable tensile strength data for ceramic materials without elaborate specimen preparation, cross bending strengths were used for comparison (Table No. VIII).

b. Thermal Expansion

Thermal expansion was measured using a silicon carbide dilatometer calibrated against a single crystal sapphire standard. These thermal expansion curves are shown for alumina, silica, Pyroceram® 9606, and Lithafrax® low expansion ceramic in Figure 17, and Table No. VIII.

c. Young's Modulus of Elasticity

Elastic modulus for each bar was measured at room temperature by sonic techniques. Since thermal shock failure occurs when the material is effectively at the starting temperature[10] elastic modulus at higher temperatures was not determined. These data are also listed in Table No. VIII.

3. Thermal Shock Resistance Factors

The thermal shock resistance of the four materials under consideration was compared on the basis of the factor $S/\alpha E$, shown in Table No. VIII. This clearly demonstrates the increased thermal shock resistance of the silica and Lithafrax® over the two materials in use at present.

4. New Materials

Several minerals are known whose thermal expansion coefficients are low, and in certain minerals, such as petalite, negative values indicating thermal contraction are known. Notable among these materials are the lithium aluminum silicates.

By using a ceramic whose thermal expansion coefficient is zero, it would be possible to produce a radome in which no thermal stresses are possible. Such a radome would be capable of resisting any thermal gradients on heating without fracture. The investigation of such bodies has received considerable attention during the last few months.

Tests were run on a number of sintered lithium aluminum silicate bodies. Thermal expansion values for these materials are quite promising but very sensitive to firing temperature, body maturity, and very slight changes in composition. The thermal expansion curves for the final matured materials are shown in Figures 18 and 19. Thermal expansion tests were run on several low expansion minerals known to have favorable thermal shock characteristics and the results are shown graphically in Figure 20. Notable are eucryptite and spodumene, both of which minerals have negative thermal expansions (Figure 21).

5. Conclusions

The work has not been carried to completion, therefore no final conclusions can be drawn. It is likely, however, that additional research in this area of low expansion ceramics will disclose compositions which will combine near-infinite thermal shock resistance together with acceptable electrical properties.

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TABLE NO. I

Spectrographic Analyses of Reactants

Material	Source of Supply and Grade	Impurities - Concentrations	
Zirconium Oxide	Carborundum Metals Co. Reactor Grade	Iron	0.1-0.5%
		Calcium	0.05-0.1%
		Silicon	0.05-0.1%
		All Others	< 0.05%
Tantalum Oxide	Fansteel Metallurgical Corporation T-400	Iron	0.1-0.5%
		Silicon	0.1-0.5%
		Niobium	0.05-0.1%
		All Others	< 0.05%
Carbon	Thermatomic Carbon Co. Thermax®	Silicon	0.1-0.5%
		All Others	< 0.05%

TABLE NO. II

Microhardness of ZrC - TaC Compositions
(Knoop, 100 gram)

Composition	Microhardness, (kg/mm^2) As Pressed 4350°F. (2400°C)	Annealed 4 Hours 3810°F (2100°C)	Annealed 4 Hours 3270°F (1800°C)	Annealed 4 Hours 2730°F (1500°C)	Density, (Percent of) (Theoretical)
ZrC	1831	-	-	-	94.7
7ZrC-TaC	2019	1743	1872	1627	86.9
4ZrC-TaC	2290	1699	1840	1745	93.0
ZrC-TaC	1888	1537	1495	1415	90.1
ZrC-2TaC	965	905	941	844	77.5
ZrC-3TaC	1595	1272	1190	1150	83.1
ZrC-4TaC	1376	-	-	-	-
ZrC-7TaC	1452	1295	1255	1163	87.1
ZrC-8TaC	1135	-	-	-	-
TaC	886, 822	820	780	808	94.2

TABLE NO. III

Electrical Resistivity of ZrC-TaC Compositions

Composition	Electrical Resistivity*, (10^{-6} ohm cm) As Pressed 1 Hour 4350°F (2400°C)	Annealed 4 Hours 3810°F (2100°C)	Annealed 4 Hours 3270°F (1800°C)	Annealed 4 Hours 2730°F (1500°C)	Density, (Percent of) (Theoretical)
7ZrC-TaC	29.8	29.2	29.3	29.3	86.9
4ZrC-TaC	31.1	30.8	29.2	30.4	93.0
ZrC-TaC	35.7	36.4	37.0	36.6	90.1
ZrC-2TaC	40.7	41.2	41.6	41.8	77.5
ZrC-3TaC	33.2	34.4	33.6	33.6	83.1
ZrC-7TaC	25.9	26.7	25.1	25.1	87.1
TaC	18.2	18.4	18.5	17.9	94.2

*Corrected to zero porosity: $R_o = R \left(\frac{1}{(1\text{-Porosity})} \right)$

TABLE NO. IV

Young's Modulus (Sonic) of ZrC - TaC Compositions

Composition	Young's Modulus (10^6 psi)					
	As Pressed 4350°F (2400°C)	Annealed 4 Hours 3810°F (2100°C)	Annealed 4 Hours 3270°F (1800°C)	Annealed 4 Hours 2730°F (1500°C)	2730°F (1500°C) Corrected for Porosity (1)	Density, (Percent of) (Theoretical)
7ZrC-TaC	51.62	52.88	53.37	54.20	66.0	91.9
4ZrC-TaC	55.52	55.69	56.49	56.58	68.3	92.2
ZrC-TaC	50.74	51.71	51.70	52.50	69.7	88.8
ZrC-2TaC	30.62	30.88	31.15	31.76	68.0	75.8
ZrC-3TaC	40.12	40.11	39.97	40.04	68.8	81.0
ZrC-7TaC	49.48	50.63	51.65	51.18	75.8	85.3
TaC	52.18	52.70	53.40	53.00	75.9	86.3

(1) $E_o = E/1-2.2\ P$ Where E_o = Young's modulus at o porosity, E is measured Young's modulus at a volume fraction porosity P.

TABLE NO. V

Melting Point Data for Refractory Metals

Material	Spectral Emissivity (0.65) at Specified Temperatures			Melting Temperatures: Observed		Window Correction		Emissivity Correction		Corrected		Literature Values	
		°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C
Niobium *	0.49[4]	Below melting point		3785	2085	45	25	360	200	4190	2310	4380	2415[4]
				3740	2060	"	"	"	"	4145	2285		
				3795	2090	"	"	"	"	4200	2315		
				3740	2060	"	"	"	"	4145	2285		
"V" shape (				4010	2210	55	30	-	-	4065	2240		
samples (				4030	2220	"	"	-	-	4085	2250		
Tantalum	0.55[5] to 0.36	80 to 5525	25 to 3025	4440	2450	65	35	790	440	5295	2925	5425	2996[4]
				4495	2480					5350	2955		
				4570	2520					5425	2995		
				4495	2480					5350	2955		
"V" shape (*	0.37			4965	2740	70	40	-	-	5035	2780		
samples (				4965	2740			-	-	5035	2780		
Molybdenum	0.42[5] to 0.328	32 to 4750	0 to 2620	3900	2150	55	30	650	360	4605	2540	4730	2610[4]
				3955	2180	"	"	"	"	4660	2570		
				3955	2180	"	"	"	"	4660	2570		
				3955	2180	"	"	"	"	4660	2570		
"V" shape (*	0.33			4260	2350	"	"	-	-	4315	2380		
samples (				4260	2350	"	"	-	-	4315	2380		
Tungsten	0.47[5] to 0.44	80 to 5115	25 to 3380	4920	2720	65	35	890	495	5880	3250	6170	3410[4]
				4935	2730					5900	3260		
				4890	2700					5845	3230		
*	0.44												

*These values used to calculate emissivity correction.

TABLE NO. VI

Measured Melting Points of Refractory Metals

Metal	Flat Sample		"V" Shape Sample	
	Average	Deviation	Average	Deviation
Tungsten	5880°F (3250°C)	± 20°F (± 10°C)	- -	- -
Tantalum	5360°F (2960°C)	± 35°F (± 20°C)	4955°F (2780°C)	± 0°F (± 0°C)
Molybdenum	4650°F (2565°C)	± 20°F (± 10°C)	4315°F (2380°C)	± 0°F (± 0°C)
Niobium	4170°F (2300°C)	± 25°F (± 15°C)	4080°F (2250°C)	± 10°F (± 5°C)

TABLE NO. VII

Melting Temperatures of ZrC-TaC Compositions

Composition	Number of Samples	Observed Melting Temperature* Average °F	Average °C	Deviation °F	Deviation °C
ZrC	8	5900	3260	45	25
7ZrC-TaC	8	6060	3350	45	25
4ZrC-TaC	5	6010	3320	115	65
3ZrC-TaC	5	6090	3365	45	25
2ZrC-TaC	4	6240	3450	25	15
ZrC-TaC	4	6340	3505	0	0
2TaC-ZrC	3	6430	3555	10	5
3TaC-ZrC	2	6520	3600	0	0
7TaC-ZrC	4	6320	3490	0	0
TaC	4	6400	3540	25	15

*Corrected for window absorption.

TABLE NO. VIII

Physical Properties of Radome Materials

Material	Alumina	Silica	Pyroceram®	Lithafrax®
Density (g/cc)	3.799	1.995	2.603	2.31
Porosity (%)	0	11.33	0	0
Young's Modulus of Elasticity (10^6 psi)	49.55	4.053	17.122	10.766
Modulus of Rupture (psi)				
Room Temperature	43,248	5,541	22,313	10,311
at 500°C		6,454	19,812	9,625
at 750°C		8,112	22,325	11,505
at 1000°C	29,787	7,998	13,924	13,231
Coefficient of Thermal Expansion (x 10^{-6}/°C)				
Room Temperature to 1000°C	8.68	0.93	6.30	2.27
$S/\alpha E$	97.5	1270.	207.	421.

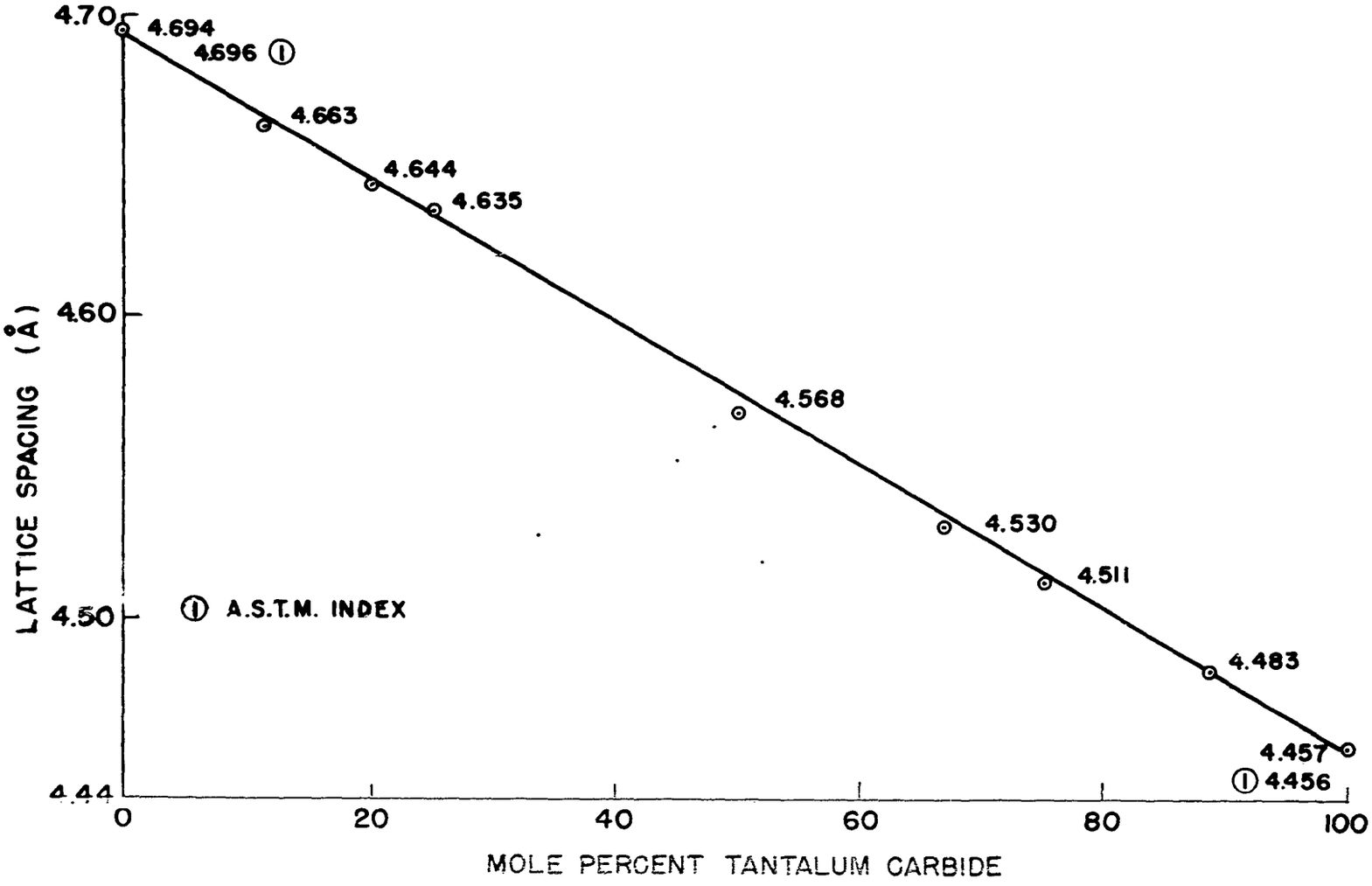


FIGURE 1

(200) LATTICE SPACINGS OF ZrC - TaC COMPOSITIONS

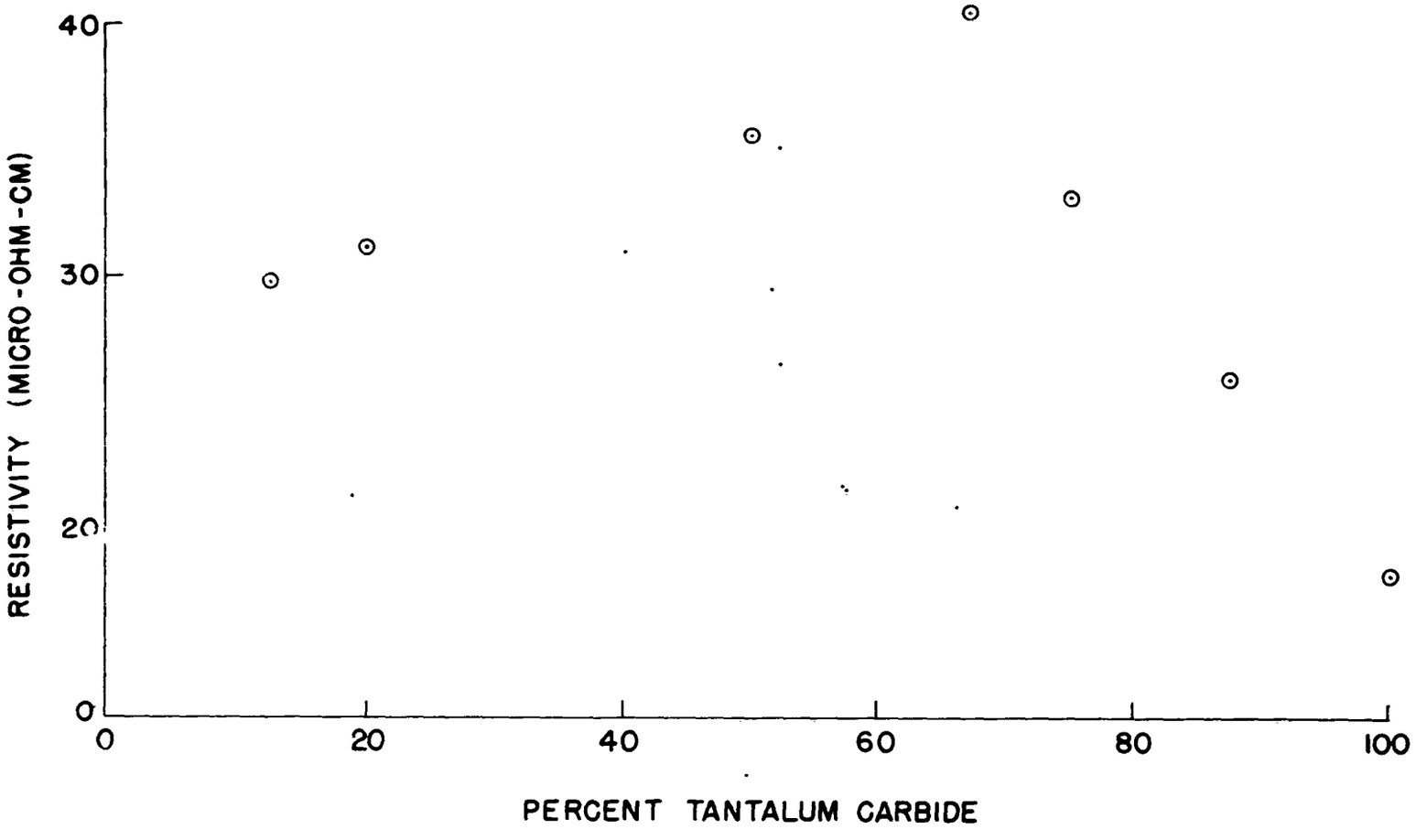


FIGURE 2

ELECTRICAL RESISTIVITY OF ZrC - TaC COMPOSITIONS
(CORRECTED FOR POROSITY)

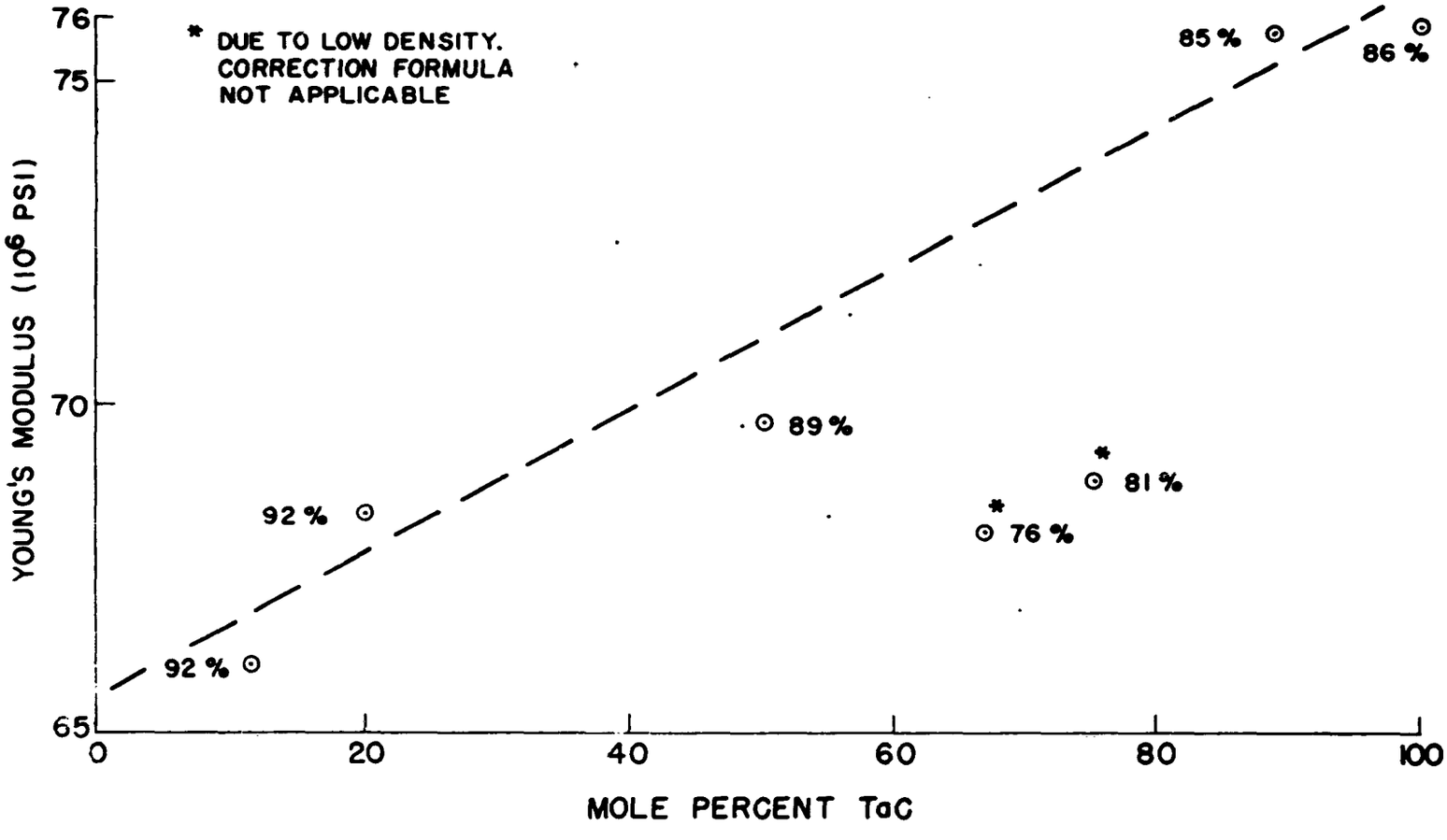
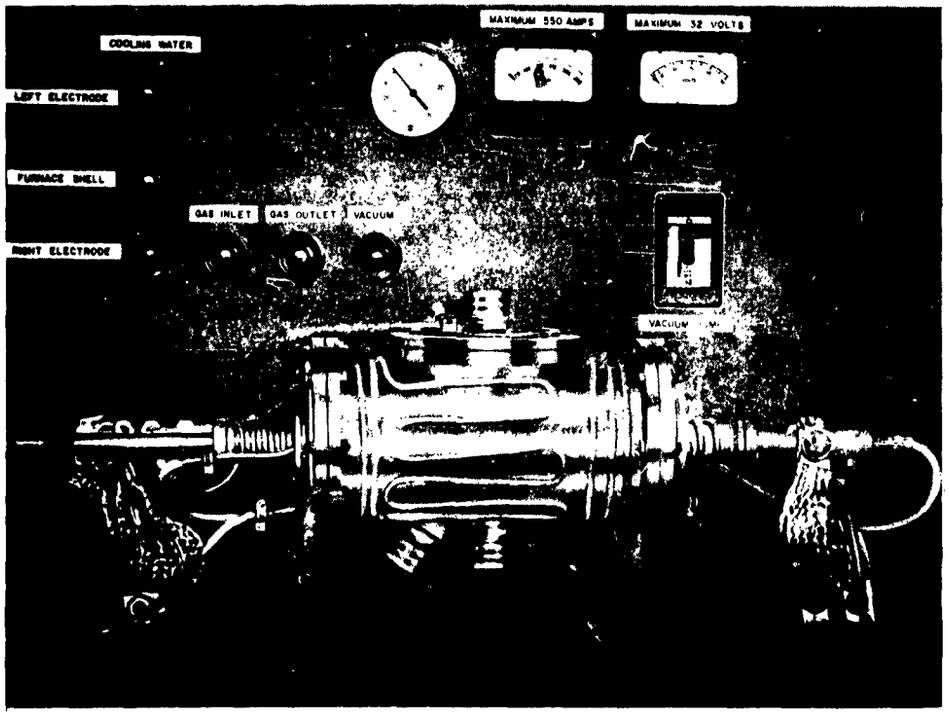
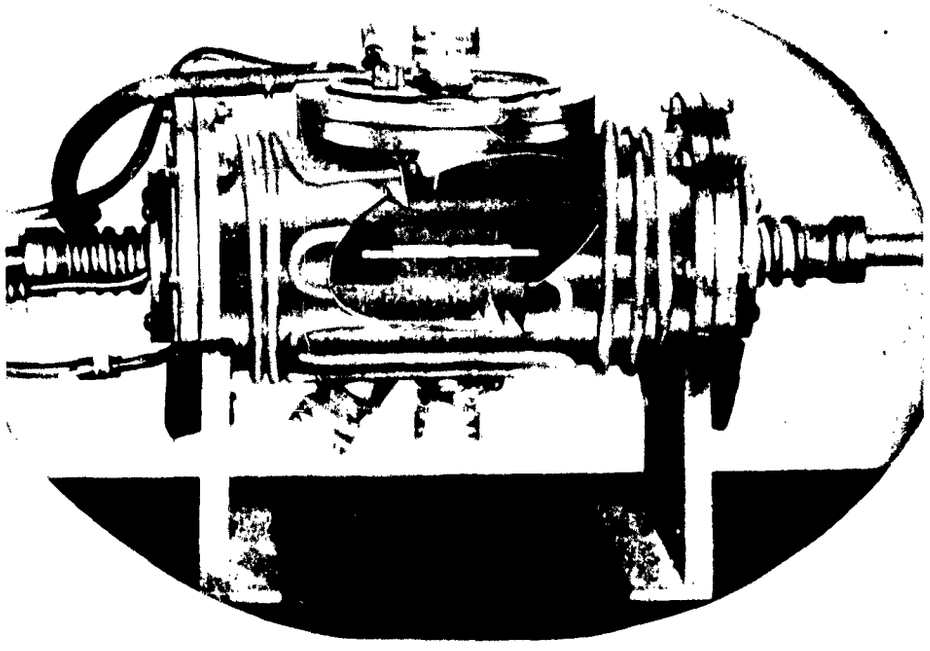


FIGURE 3

YOUNG'S MODULUS OF ZrC - TaC COMPOSITIONS
(CORRECTED FOR POROSITY)



4 High Temperature Resistance Furnace



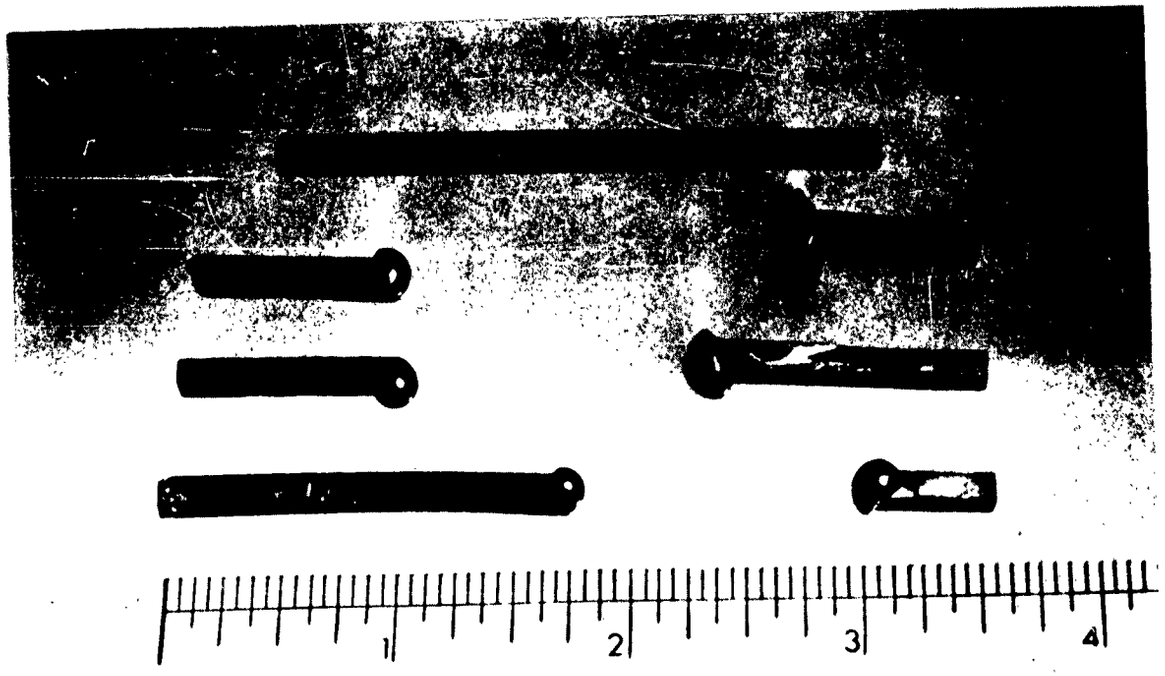


Plate No. 8184

Figure 5 - Zirconium Carbide Samples.

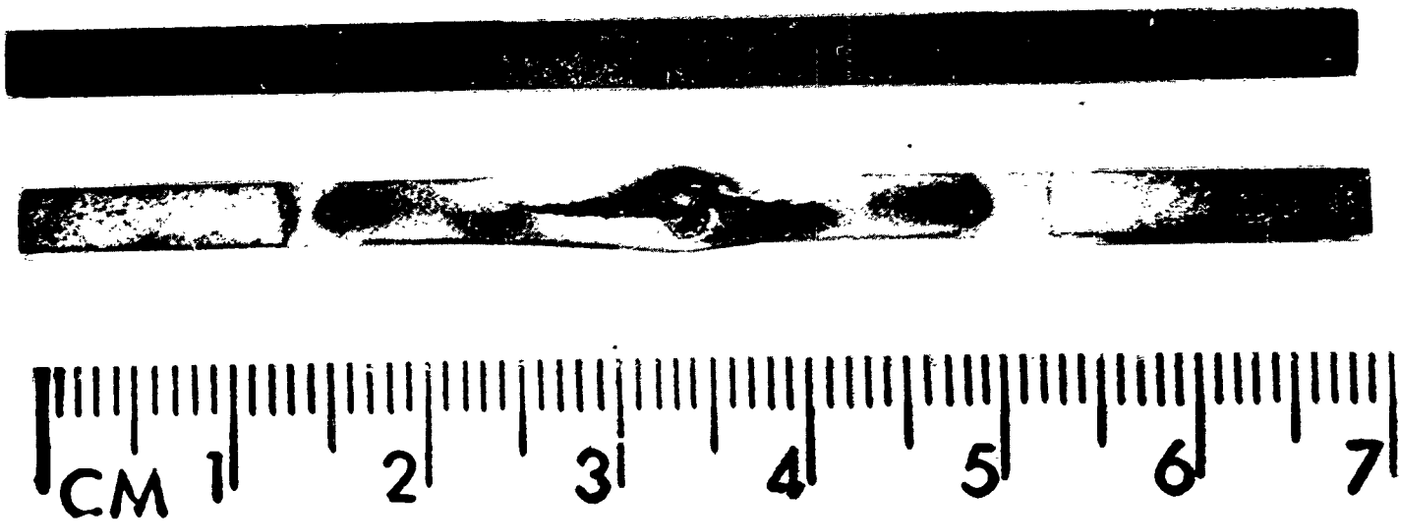


Plate No. 8324

Figure 6 - Zirconium Carbide Melting Point Samples.
a. Before heating
b. Heated through inversion, note splitting

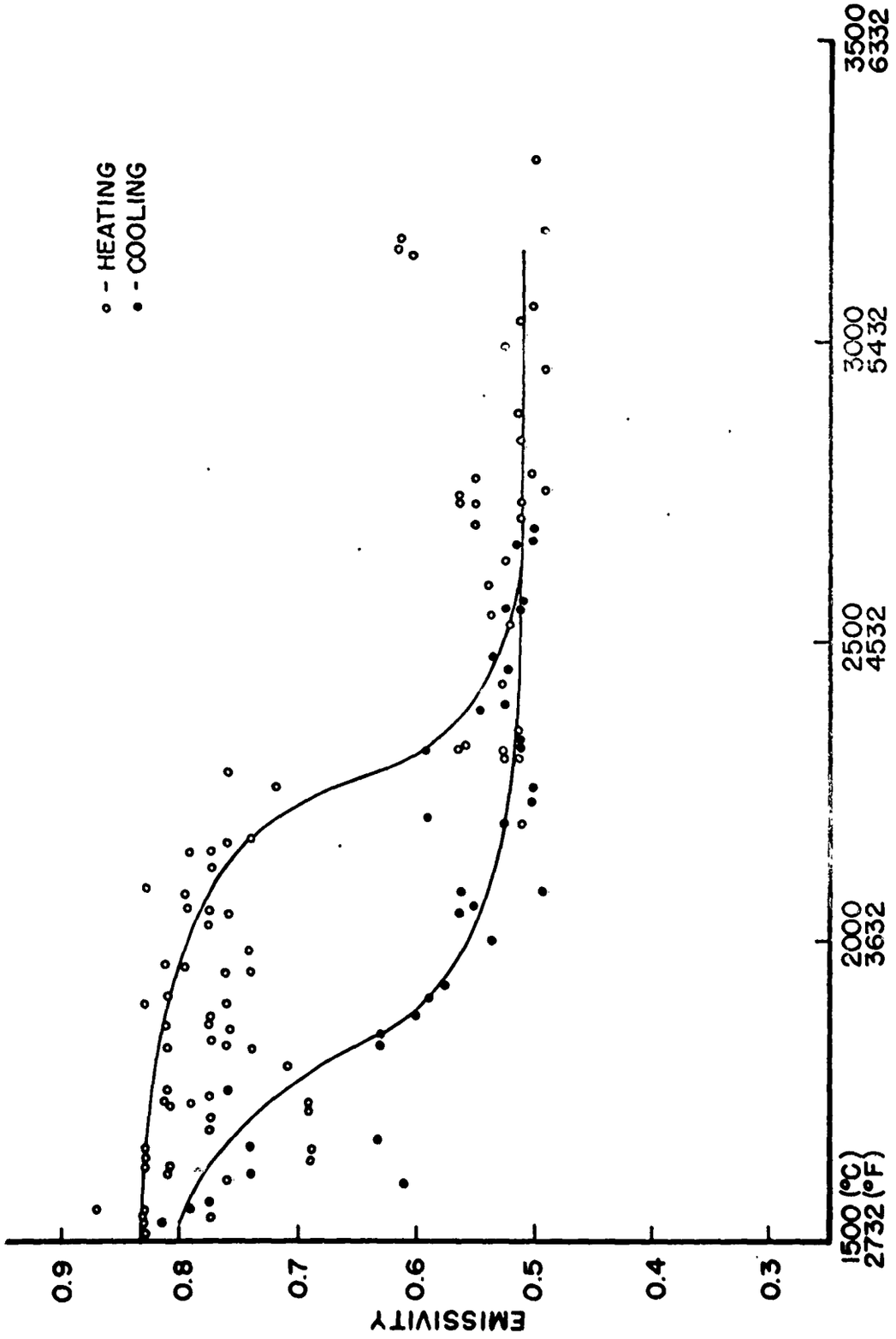


FIGURE 7

SPECTRAL EMISSIVITY OF ZrC AT 0.65 μ

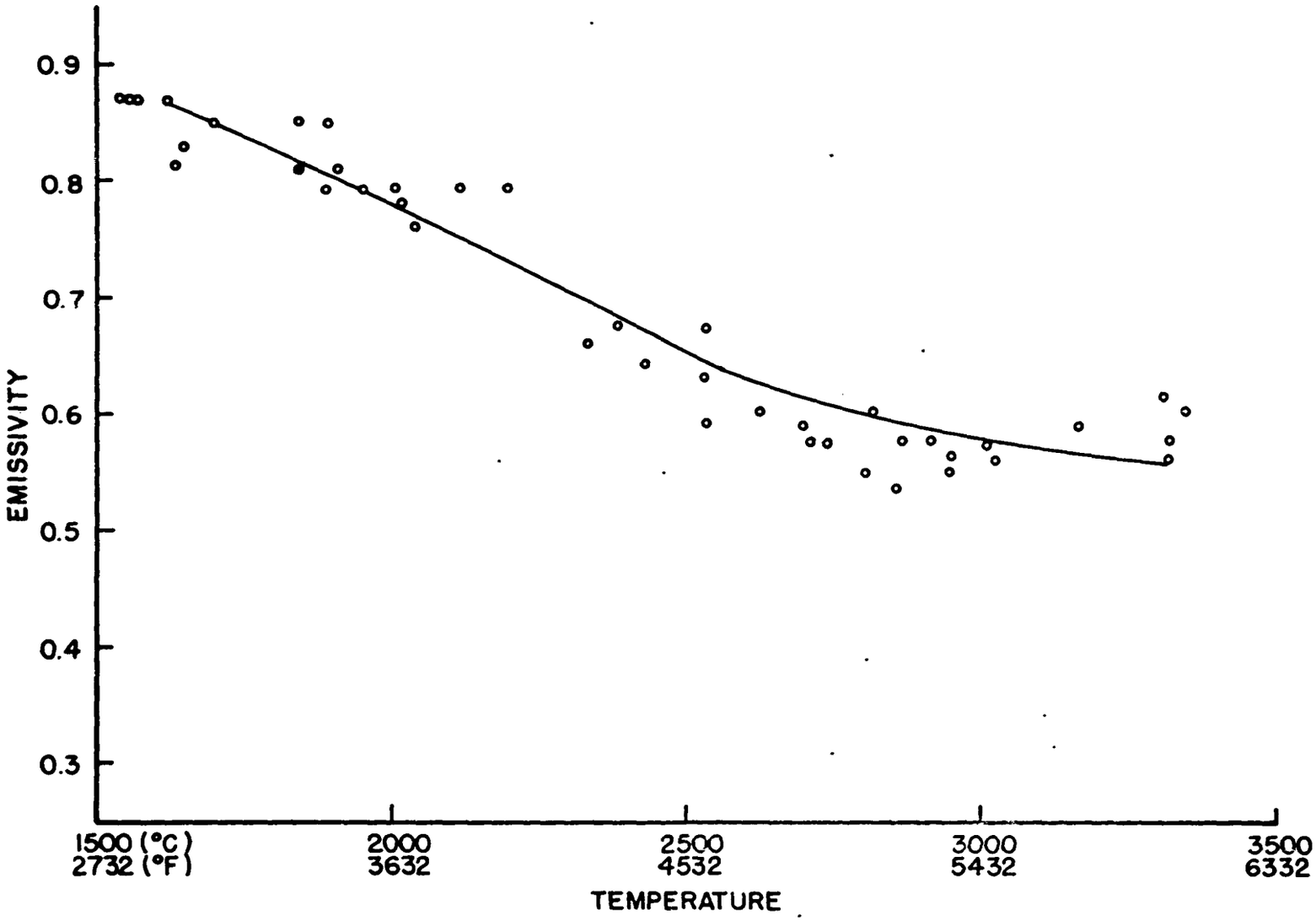


FIGURE 8

SPECTRAL EMISSIVITY OF
7 ZrC - TaC AT 0.65 μ

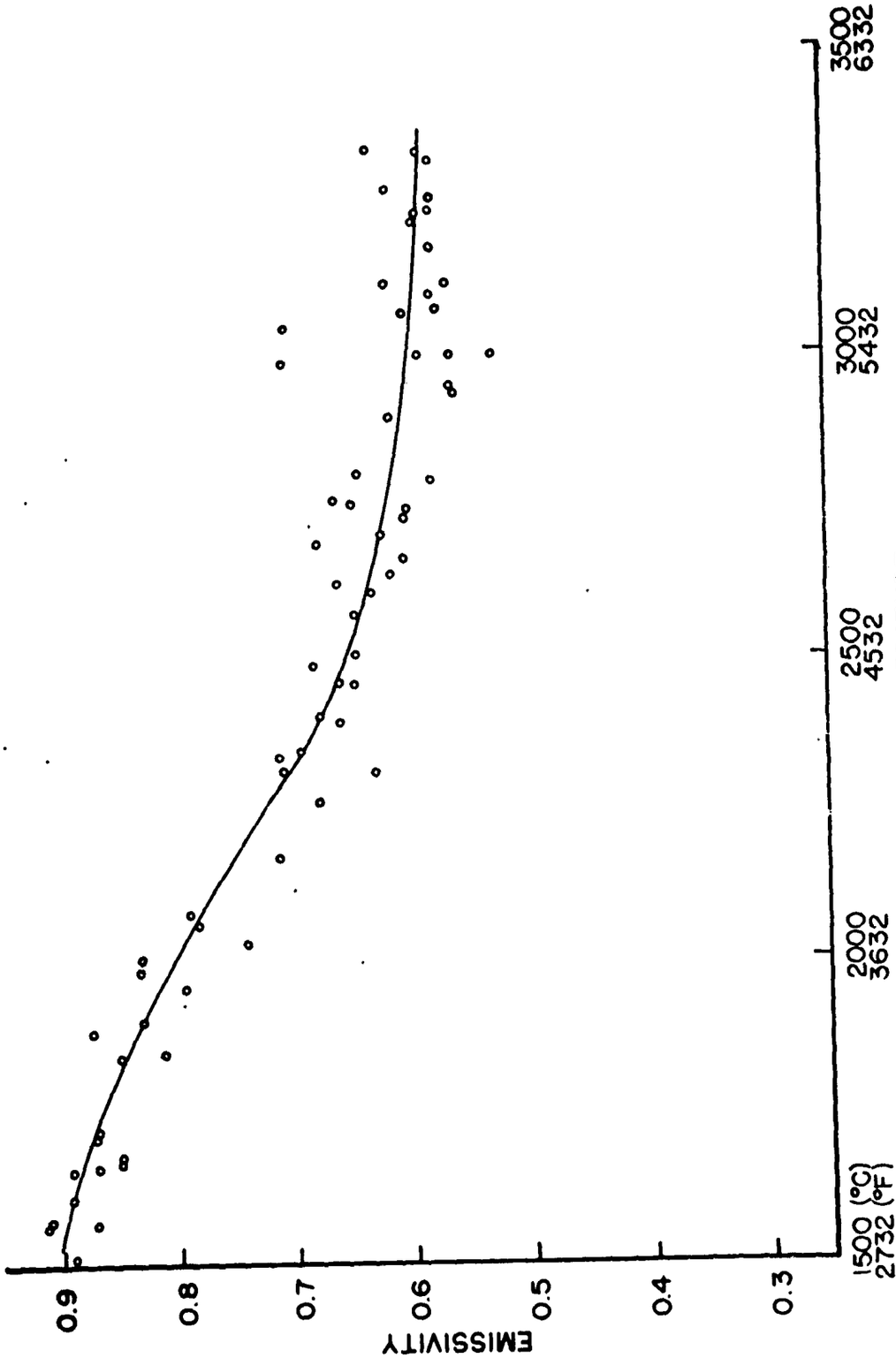


FIGURE 9

SPECTRAL EMISSIVITY OF
4 ZrC - TaC AT 0.65 μ

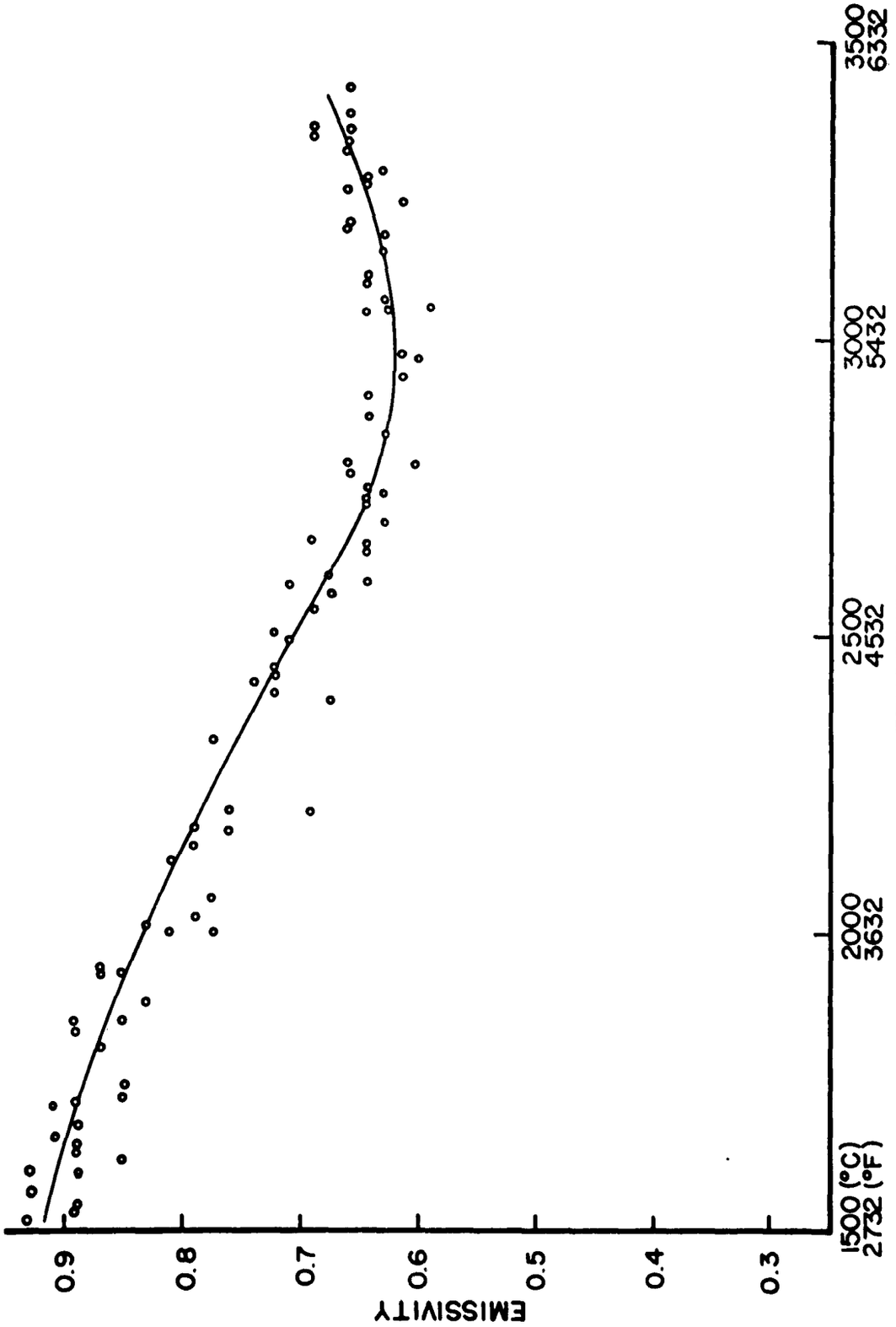


FIGURE 10

SPECTRAL EMISSIVITY OF 3 ZrC - TaC AT 0.65 μ

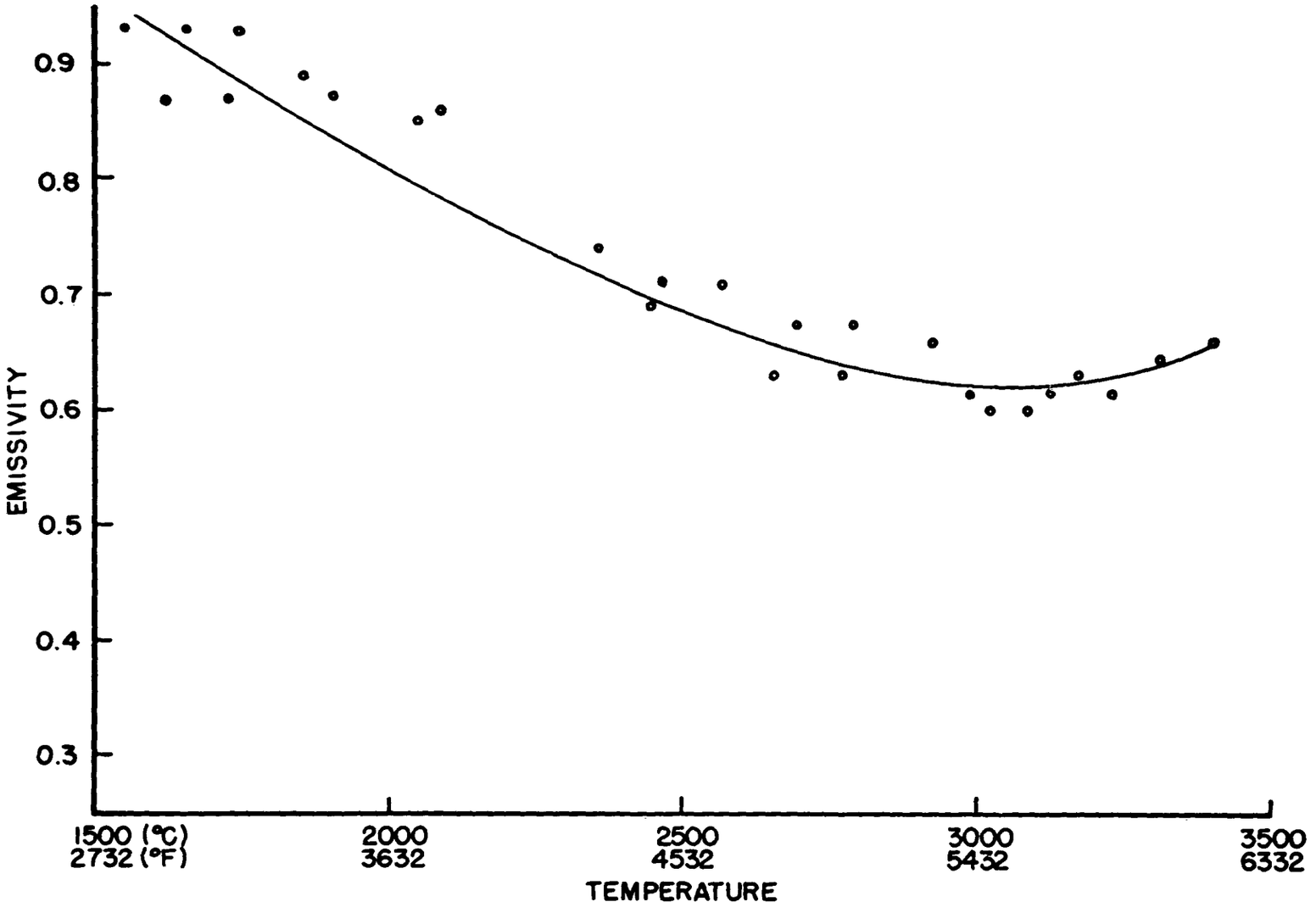


FIGURE 11

SPECTRAL EMISSIVITY OF
TaC - ZrC AT 0.65 μ

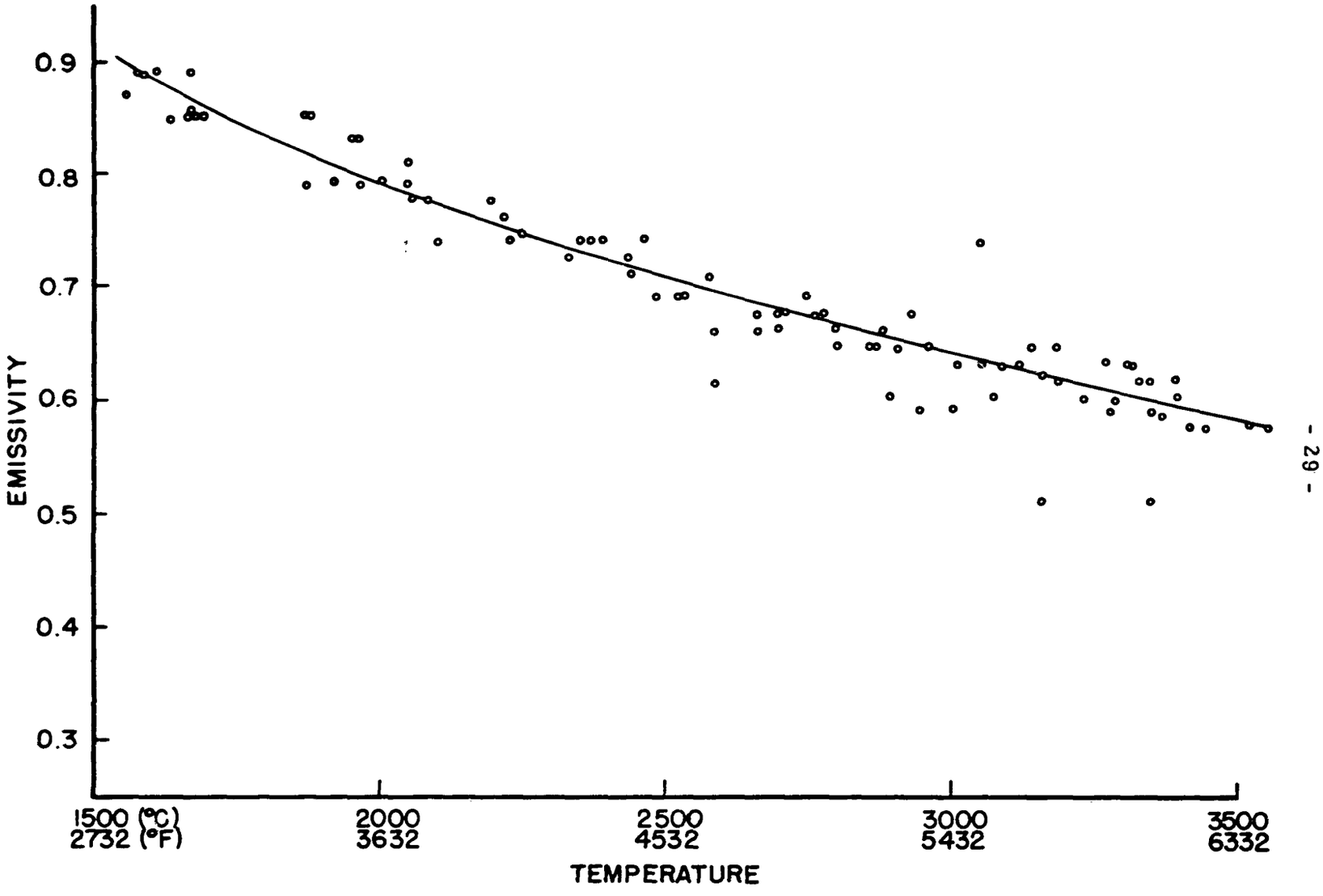


FIGURE 12

SPECTRAL EMISSIVITY OF
2 TaC - ZrC AT 0.65 μ

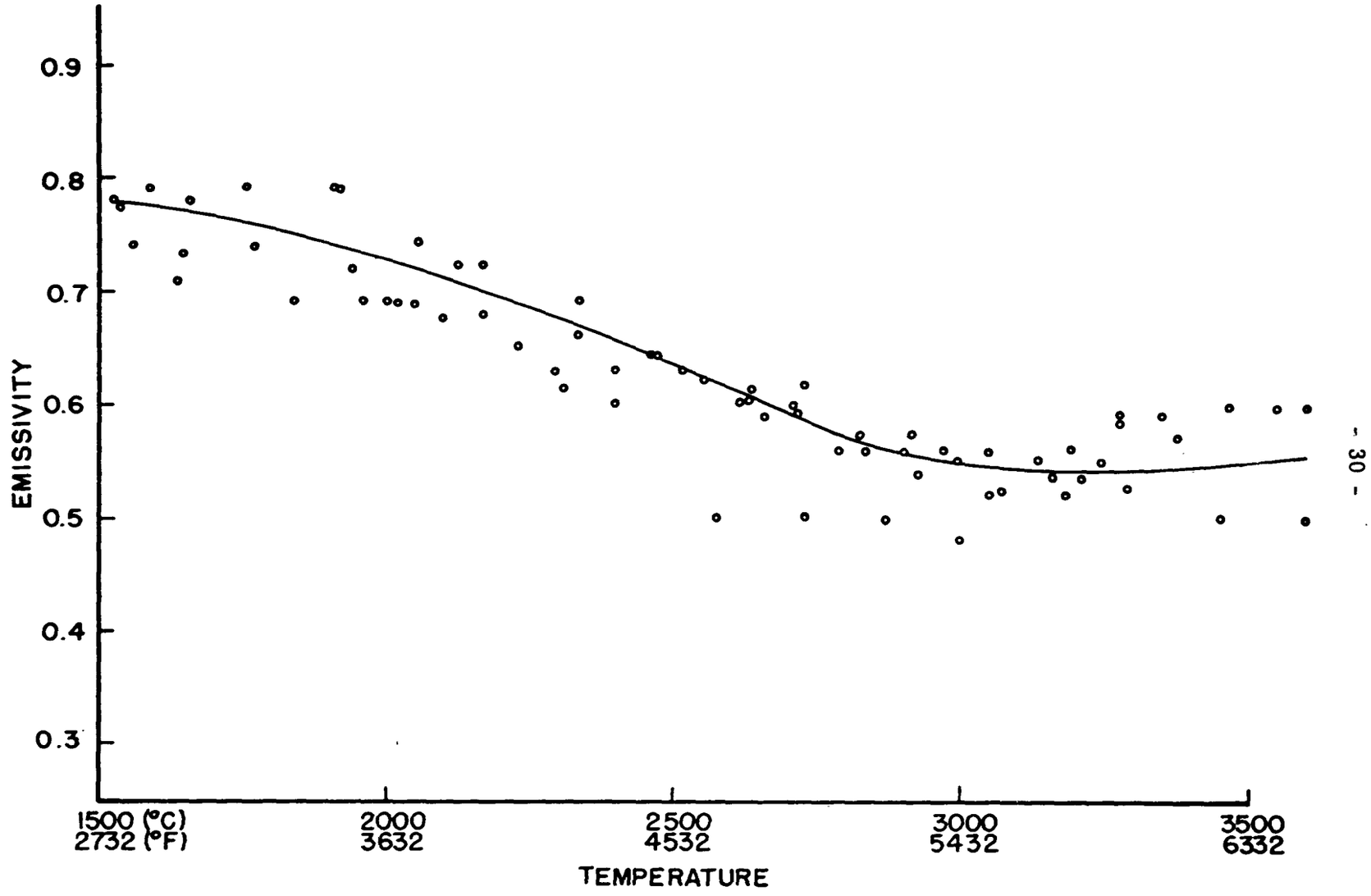


FIGURE 13

SPECTRAL EMISSIVITY OF
3 TaC - ZrC AT 0.65 μ

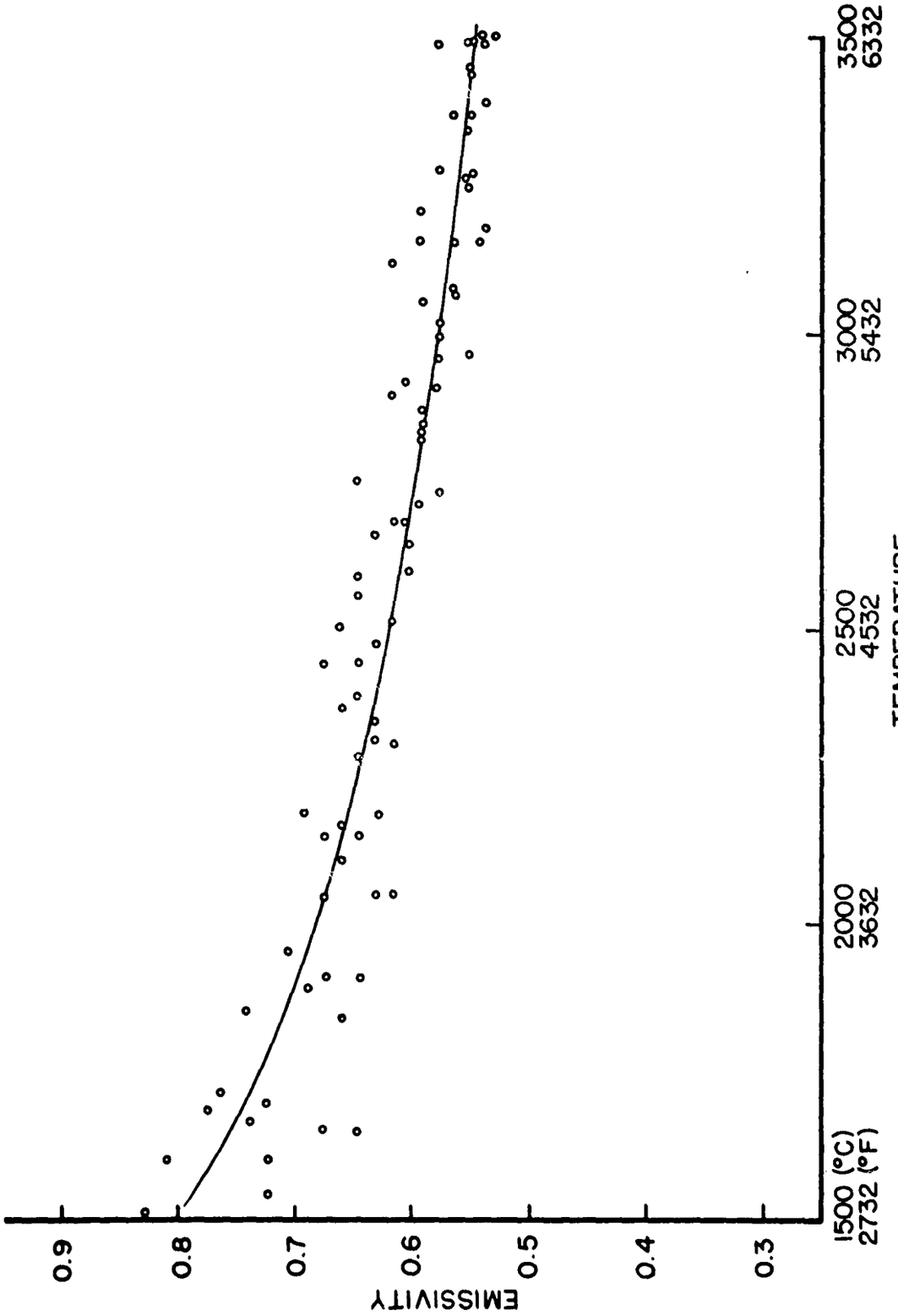


FIGURE 14

SPECTRAL EMISSIVITY OF 7 TaC - ZrC AT 0.65 μ

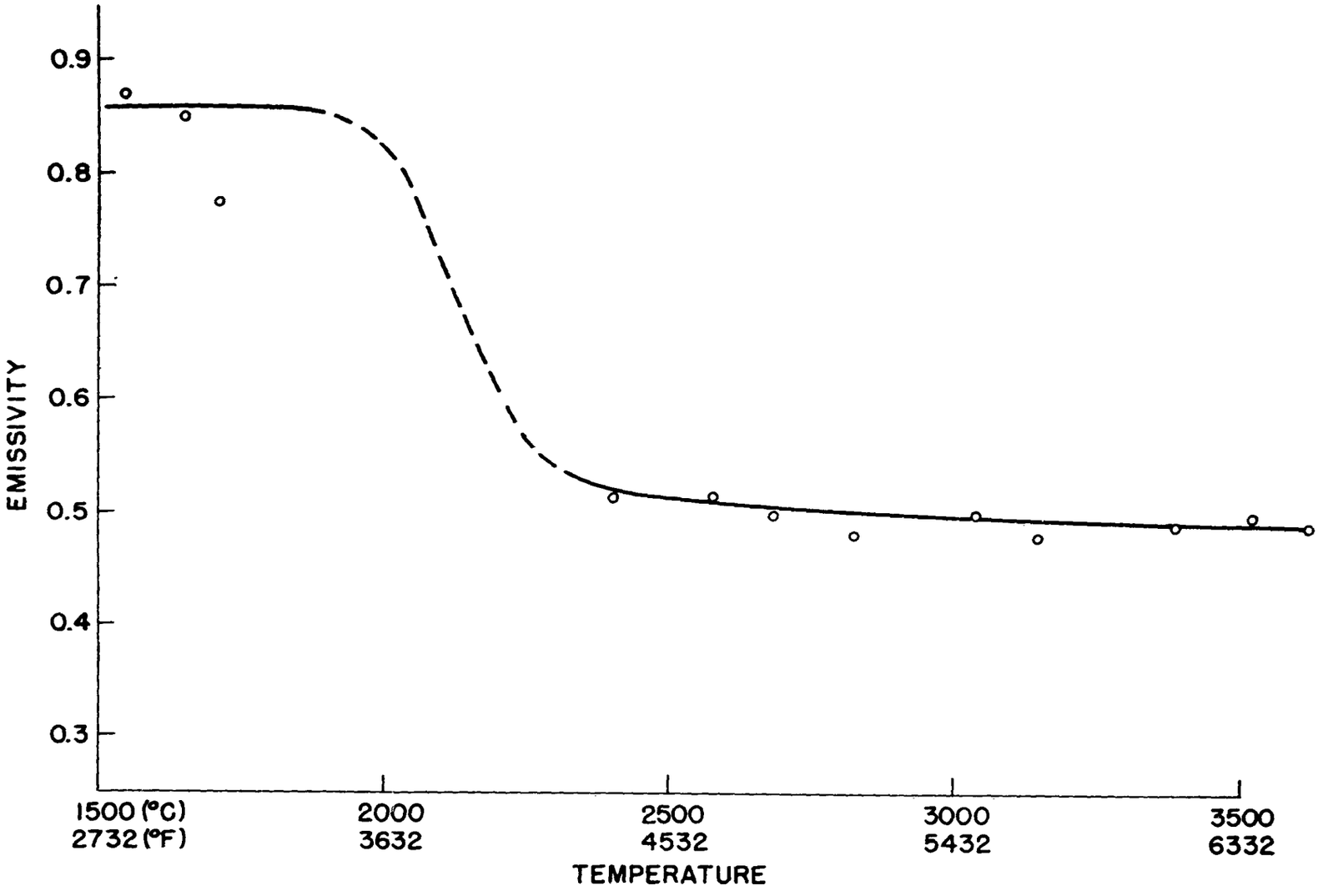


FIGURE 15

SPECTRAL EMISSIVITY OF TaC AT 0.65 μ

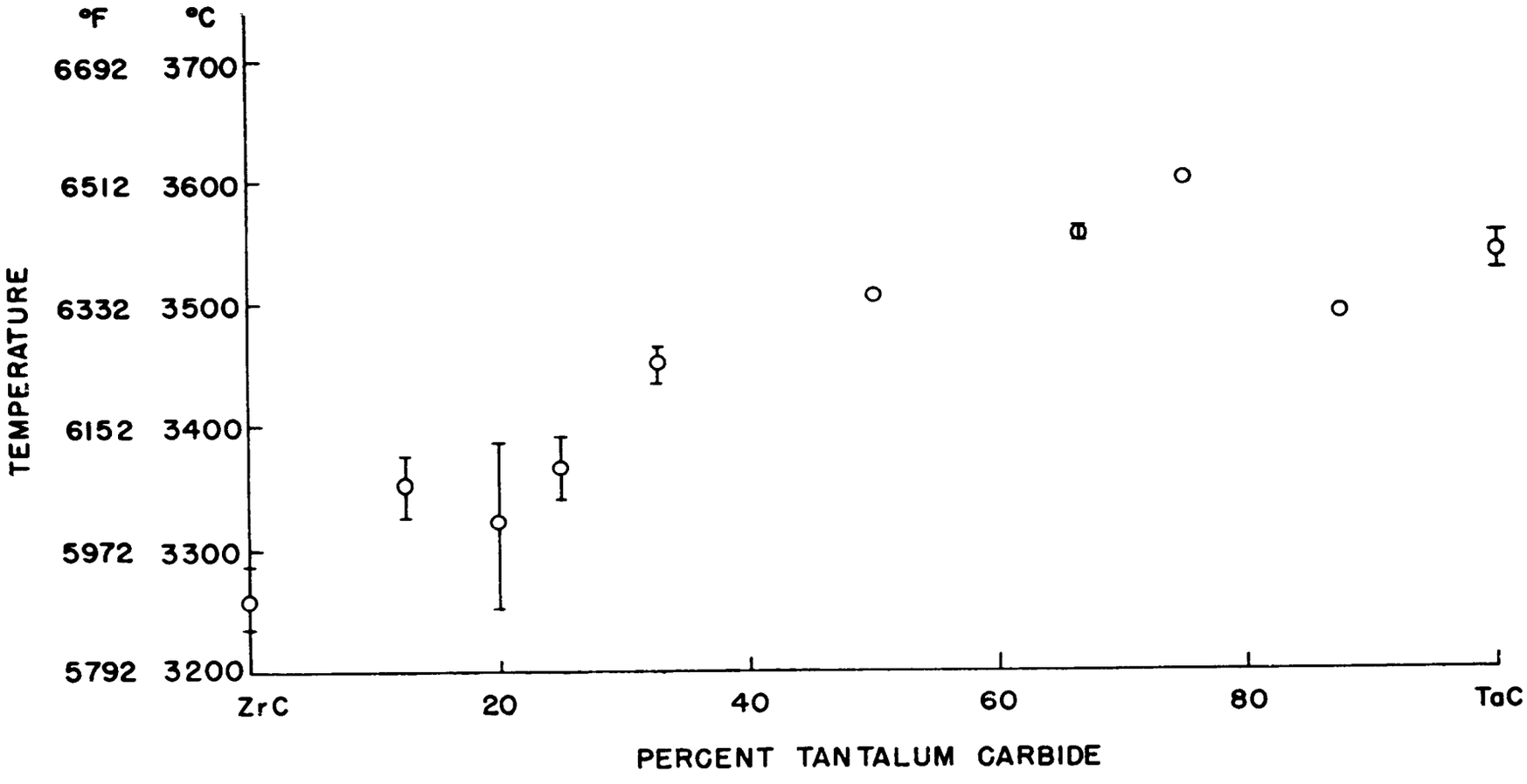


FIGURE 16

MELTING TEMPERATURE OF ZrC - TaC COMPOSITIONS

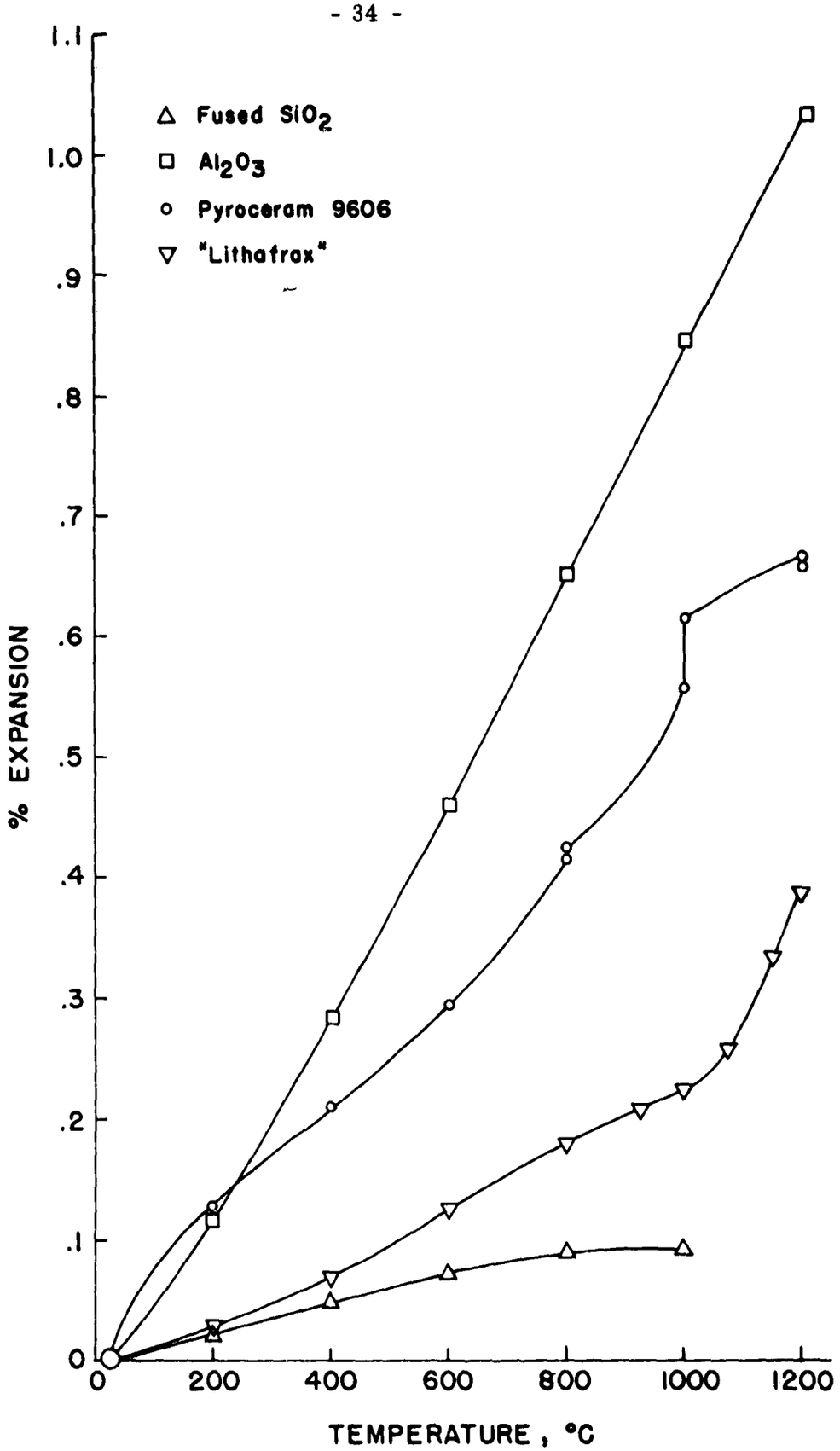


FIGURE 17

THERMAL EXPANSION OF RADOME MATERIALS

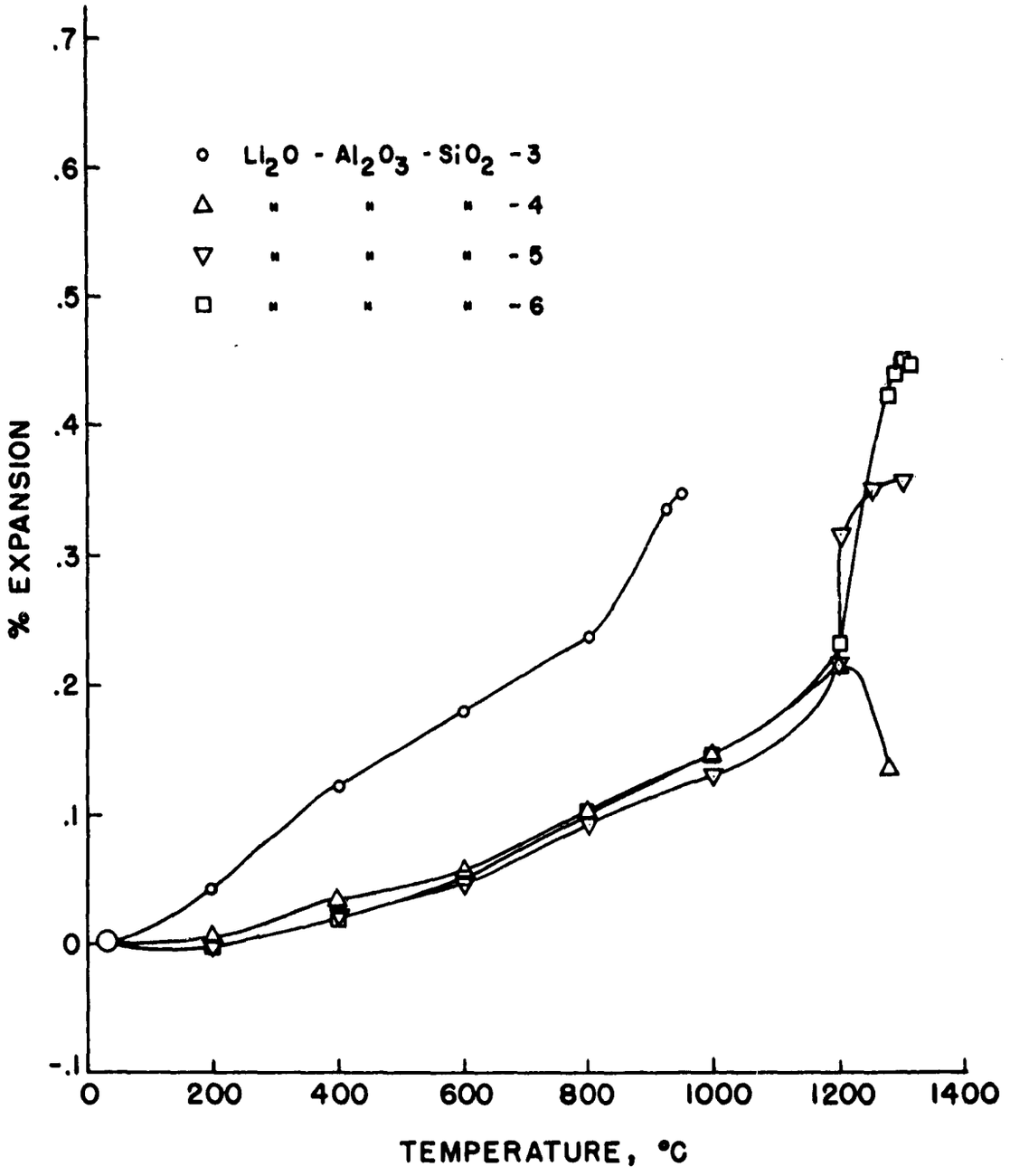


FIGURE 18

THERMAL EXPANSION OF $Li_2O - Al_2O_3 - SiO_2$ COMPOSITIONS

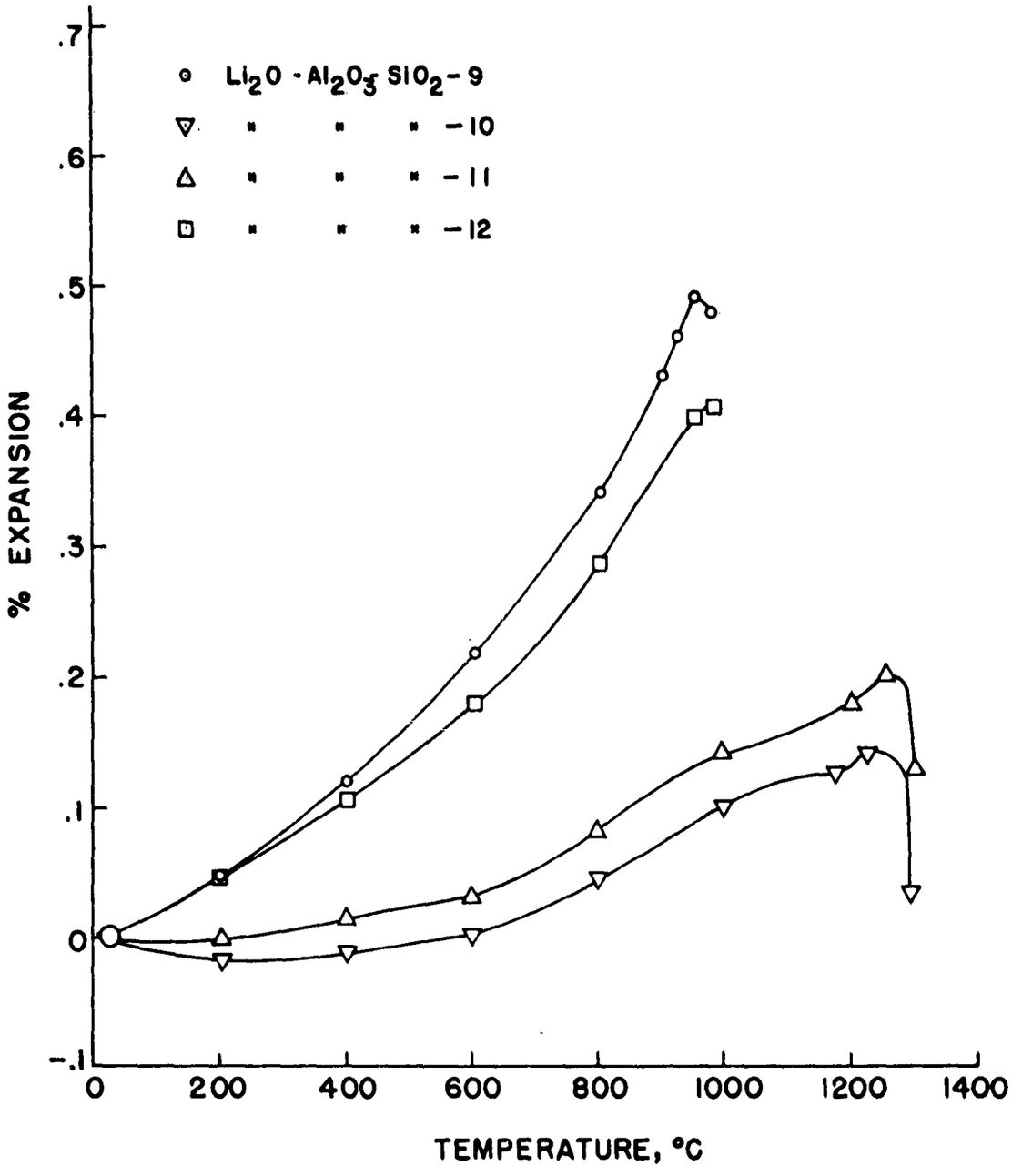


FIGURE 19

THERMAL EXPANSION OF $Li_2O - Al_2O_3 - SiO_2$ COMPOSITIONS

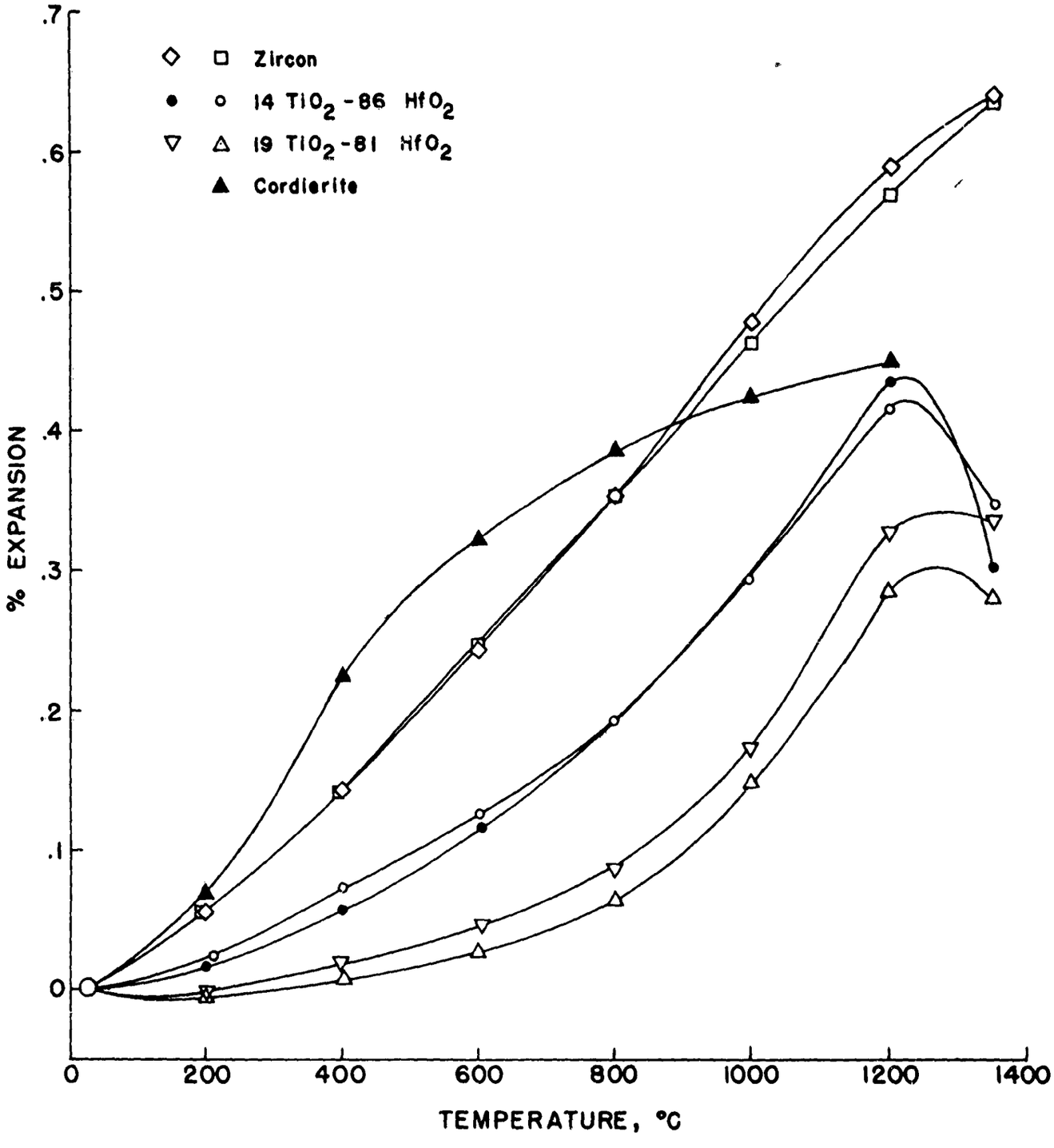


FIGURE 20

THERMAL EXPANSION OF LOW EXPANSION MINERALS

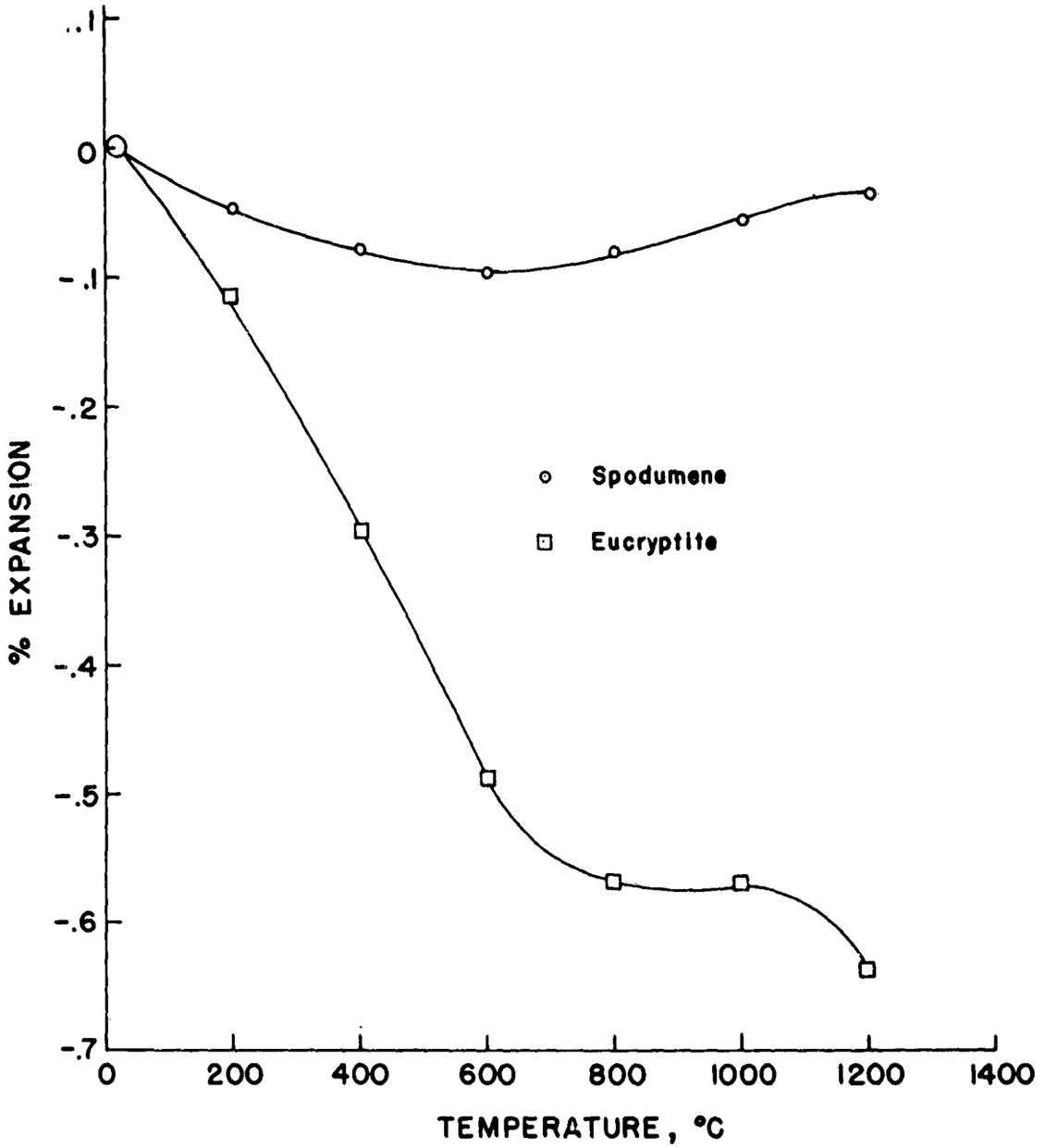


FIGURE 21

THERMAL EXPANSION OF NEGATIVE EXPANSION MINERALS

APPENDIX A

CALCULATION OF TEMPERATURE CORRECTION FOR WINDOW ABSORPTION

The Vycor® window (1/8" thick) used throughout the study introduced an error in observed temperature, which was corrected as follows.

The formula to correct for absorption by a window is:

$$\frac{1}{T_{true}} - \frac{1}{T_{apparent}} = \frac{\lambda}{C_2} \log e^{-ut} \qquad (1)$$

Where T_{true} = true temperature (^{o}K)
$T_{apparent}$ = the measured temperature (^{o}K)
λ = wavelength of light used (in microns)
C_2 = constant
u = coefficient of absorption of sight glass
t = thickness of sight glass

Equation (1) may be reduced to

$$\frac{1}{T_{true}} - \frac{1}{T_{apparent}} = \frac{0.65\ ut}{14,320} \qquad (2)$$

Since all factors on the right are constants for a particular series of temperature measurements, it becomes

$$\frac{1}{T_{true}} - \frac{1}{T_{apparent}} = K \qquad (3)$$

Knowing any pair of true and apparent temperatures, it becomes possible to correct all others for window absorption.

To verify constancy of this equation (3), a series of temperature measurements were made over the range 1000 - 2700°C. From these were calculated the constant K, which was then averaged over 500° intervals. The following table presents these data and calculated values.

True Temperature		Apparent Temperature		K
^{o}C	^{o}K	^{o}C	^{o}K	$(10^{-8}/^{o}K)$
995	1269	988	1261	438
1050	1323	1041	1314	518
1116	1389	1106	1379	522
1166	1439	1157	1430	438
1209	1482	1199	1472	458
1285	1558	1276	1549	373
1328	1601	1318	1591	393
1364	1637	1355	1628	338
1427	1700	1415	1688	418
1490	1763	1475	1748	479
	(Average:	1000 - 1500^{o}C		437 x $10^{-8}/^{o}$K)
1548	1821	1534	1807	426
1607	1880	1593	1866	400
1656	1929	1640	1913	433
1697	1970	1680	1953	442
1765	2038	1748	2021	412
1800	2073	1780	2053	470
1850	2123	1830	2103	448
1905	2178	1885	2158	426
1975	2248	1950	2223	500
	(Average:	1500 - 2000^{o}C		440 x $10^{-8}/^{o}$K)
2052	2325	2025	2298	505
2110	2383	2082	2355	500
2180	2453	2155	2428	420
2240	2513	2215	2488	400
2330	2603	2300	2573	448
2420	2693	2395	2668	348
	(Average:	2000 - 2500^{o}C		436 x $10^{-8}/^{o}$K)
2500	2773	2475	2728	330
2616	2889	2580	2853	437
2715	2988	2670	2943	511
	Average:	2500 - 2750^{o}C		426 x $10^{-8}/^{o}$K)

The value used for all window corrections with the particular Vycor® window was the rounded average of the calculated values: 435 x $10^{-8}/^{o}$K. Such a correction, applied to an observed temperature of 3500^{o}C leads to a corrected value of 3563^{o}C.

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